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THE UV PHOTOCHEMISTRY OF $C_2 N_2$

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ABSTRACT

The absorption, emission and photodissociation yield spectra of $C_2 N_2$ have been measured in the 220 and 210 nm region near the 4_0^1 and $1_0^1 4_0^1$ bands of the $A^1\Sigma^- \leftarrow X^1\Sigma^+$ system. The emission spectrum showed very few lines which appeared in the absorption spectrum. Moreover the emission had 660 ns lifetime and, at 210 nm a very large electronic emission quenching rate. We used laser induced fluorescence to measure the relative yield of CN radicals as a function of photolysis wavelength. This spectrum seemed to follow the absorption spectrum below the dissociation threshold. Energy in the CN fragments appeared to be statistically distributed.

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Introduction

Cyanogen is a photochemically important molecule found in the atmosphere of Titan, and perhaps in other astronomical systems. We have discovered that this molecule has a strong and distinctive emission spectrum that can be used for remote detection.

Cyanogen is also an extremely simple tetra-atomic system in which predissociation can be studied. Potential energy surfaces have been calculated for all of the excited states which means that models of dissociation dynamics can be tested in detail.

Experimental

The apparatus was similar to that described in Reference [1]. $C_2 N_2$ from Matheson was purified by freeze-thaw cycling. The gas flow from a 3 liter reservoir was controlled by a Granville-Phillips fine metering valve and introduced into the cell through a hypodermic needle. The pressure was monitored by a MKS Model 200 capacitance manometer of a cold cathode gauge.

The excitation source was a Spectra Physics PDL-2 dye laser pumped by a DCR-11 Nd-YAG system. Light from the dye laser was frequency doubled in a KDP crystal and Raman shifted in about 10 atmospheres of hydrogen gas. For this experiment third and fourth anti-Stokes shifted beams were used. Since the doubled light is 100% polarized, all of the Raman shifted beams will be fully polarized. The intensity of the dye laser beam ranged between 25 and 60 μJ depending on the dye gain curve and dye used. The energy contained in each pulse of the photolysis beam ranged from a few to perhaps a hundred microjoules.

Emission from $C_2 N_2$ was detected directly through an unfiltered 11 stage EMR VUV photomultiplier. The signal was integrated by a PAR Model 160 boxcar analyzer.

CN fragments were detected by laser-induced fluorescence (LIF) excited by Molectron DL-II dye laser pumped by UV400 Nitrogen laser. The roughly 200 μJ beam was expanded, attenuated by neutral density glass filters and passed through a thin film glass polarizer to eliminate any elliptical character. Care was taken that the LIF signal was unsaturated. The electric vector of this dye laser beam was parallel to that of the photolysis laser. The overlapping laser beams passed through the experimental cell in opposite directions. The LIF signal was monitored about 100 μs after the photolysis pulse. This delay eliminates the effect of any changes in the nascent CN distribution as the photolysis wavelength was changed. The nitrogen pumped dye laser was tuned to resonance with the $R(7)$ line of the CN $B^2\Sigma^+ \leftarrow X^2\Sigma^+$ violet system. LIF was monitored by an EMI 9558 photomultiplier tube looking through a 388 nm bandpass filter. The photomultiplier was placed perpendicular to the plane of the laser beams and the electric vector of the photolyzing light. The fluorescence signal was integrated in one channel of a PAR Model 162 boxcar analyzer. The intensity of the dye laser beam was measured by picking off a reflection and sending it into a photodiode.

The experiments were controlled by an IBM PCXT microcomputer based data acquisition system constructed in our laboratory. The firing of the lasers and the dye laser scanning was controlled by the microcomputer.

Absorption spectra were measured directly on a Cary 2390 UV-VIS-NIR spectrophotometer or by measuring the far UV light intensity before and after the cell using scintillators to convert the light frequency into regions that can be detected by two Si photodiodes.

Results

Figure 1 shows an absorption spectra measured on the Cary 2390 spectrophotometer between 200 and 230 nm. The lower half of the diagram shows the difference between spectra measured at 20 and 70°C when the cell was heated by water from a thermostated bath. This identifies lines that originate in excited vibrational states and aids in the assignment of the vibrational bands. Figure 2 shows an absorption spectrum taken in the 220 nm region with a higher resolution instrument [2].

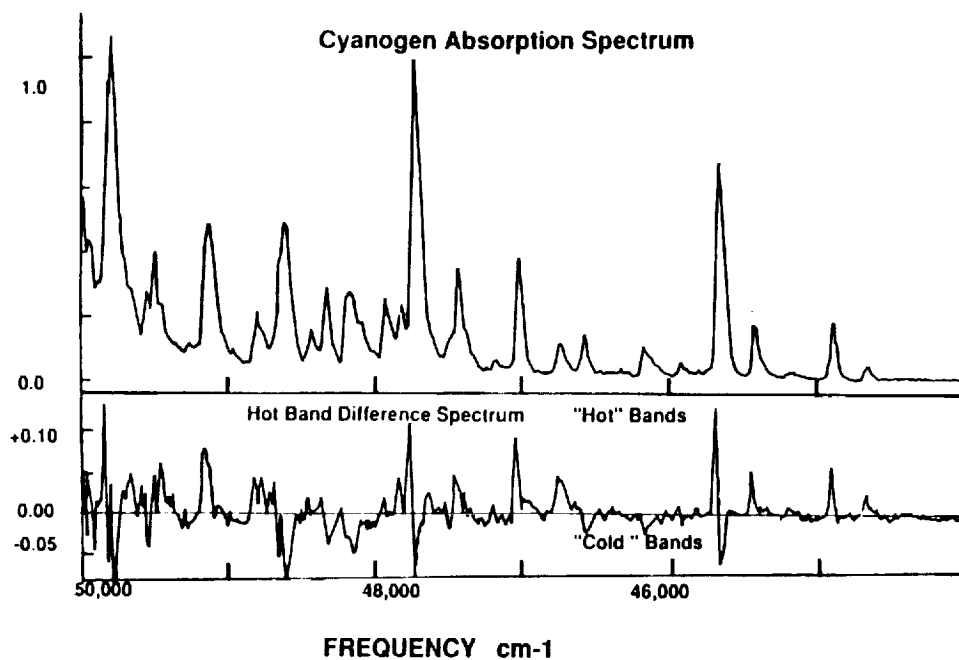


Figure 1

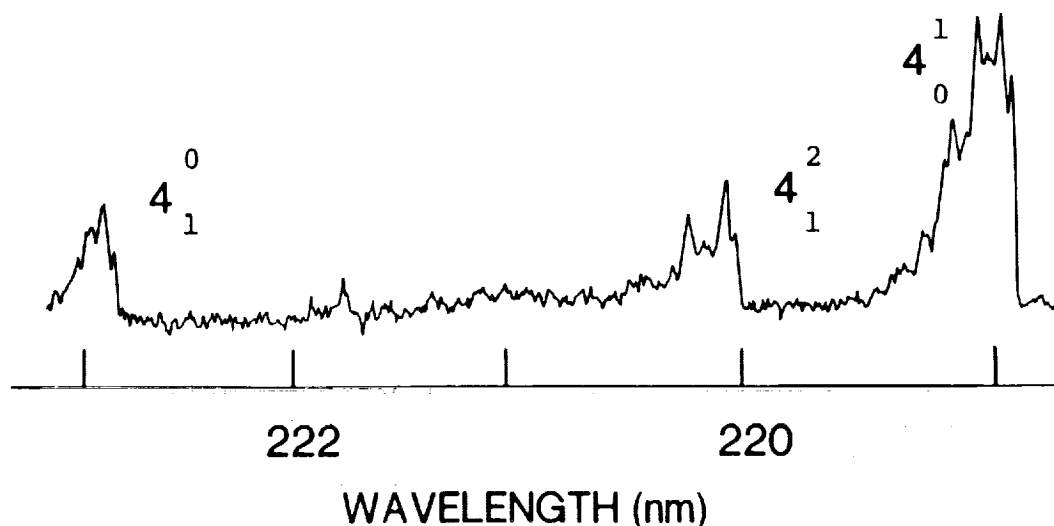


Figure 2

Figure 3 shows the spectrum of total emission following laser excitation in the 220 nm region. Attempts to detect CN fragments from photodissociation were unsuccessful although we were able to detect fragments if we used the much weaker 200 nm fourth anti-Stokes beam. This confirms the bond energy measurements of Eres and McDonald [3] which predicted that the dissociation threshold would be 212.76 nm. The emission spectrum does not match the absorption spectrum in all detail. The ratio of intensities between the 4_0^1 and 4_1^2 bands is somewhat different from that seen in absorption as is the shape of the bands. The emission lifetime obtained at the peak of the 4_0^1 band is 660 ns. Figure 4 shows the fluorescence spectrum obtained when the dye laser is fixed on the Q bandhead of the 4_0^1 line.

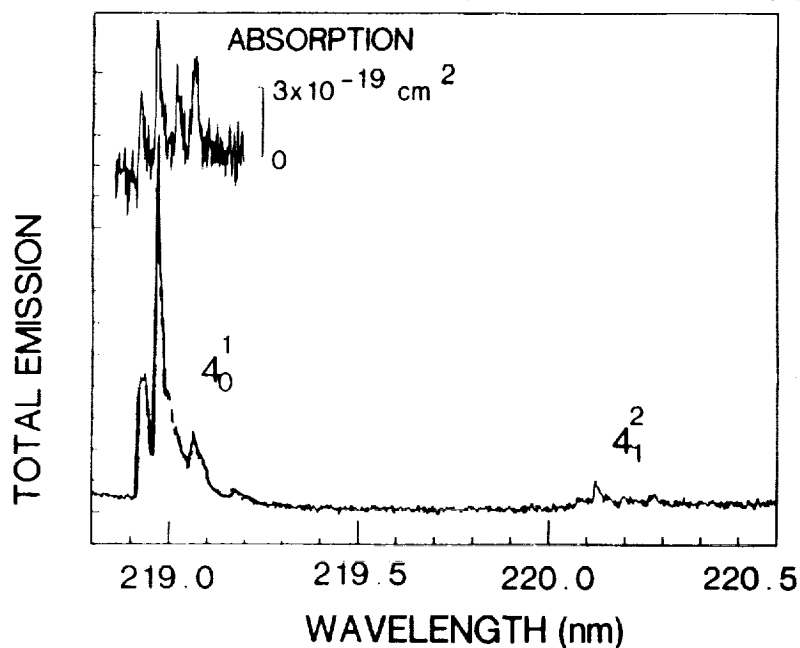


Figure 3

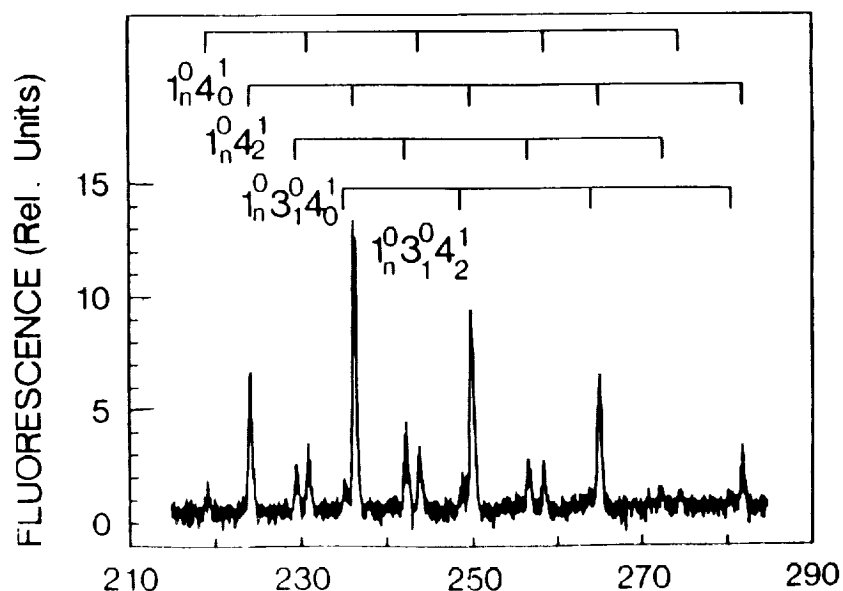


Figure 4

Figure 5 shows the absorption spectrum measured between 206.4 and 211 nm. Figure 6 shows the yield of CN fragments in the same region. The relative yield of CN was measured as a function of photolysis wavelength by (LIF). The photolysis yield generally follows the absorption spectrum as would be expected in any predissociation. Figure 7 shows the emission spectrum measured in the same region. Only a few peaks are observed. Note that the signal from the $1_0^0 4_0^1$ band extends far above the top of the scale. The insert in Figure 7 shows the $1_0^0 4_0^1$ band attenuated by a factor of 50. Structure can be seen on the red side of the emission at higher gain. We have measured the lifetimes of the emission excited in this band as a function of pressure. A Stern-Volmer plot of the measured decay rates is shown in Figure 8.

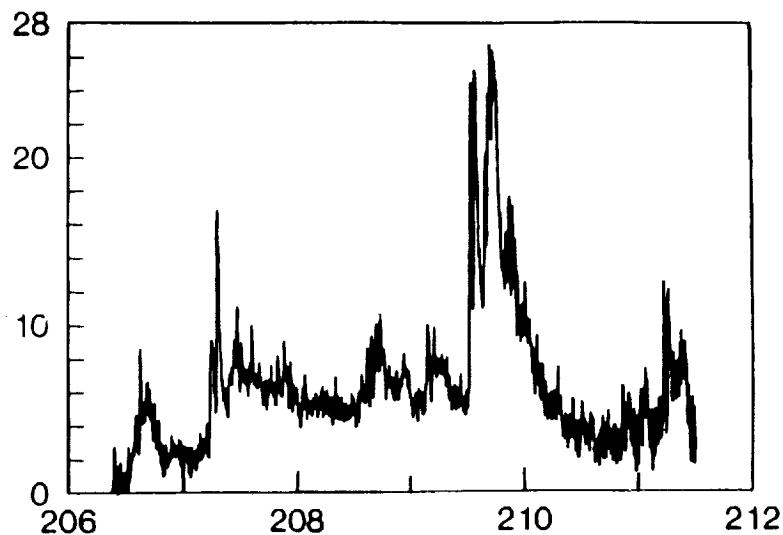


Figure 5

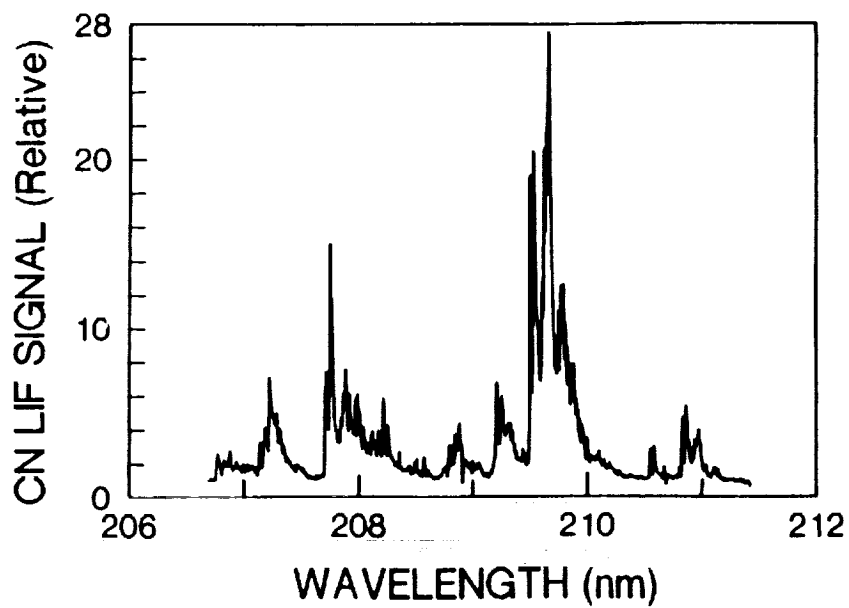


Figure 6

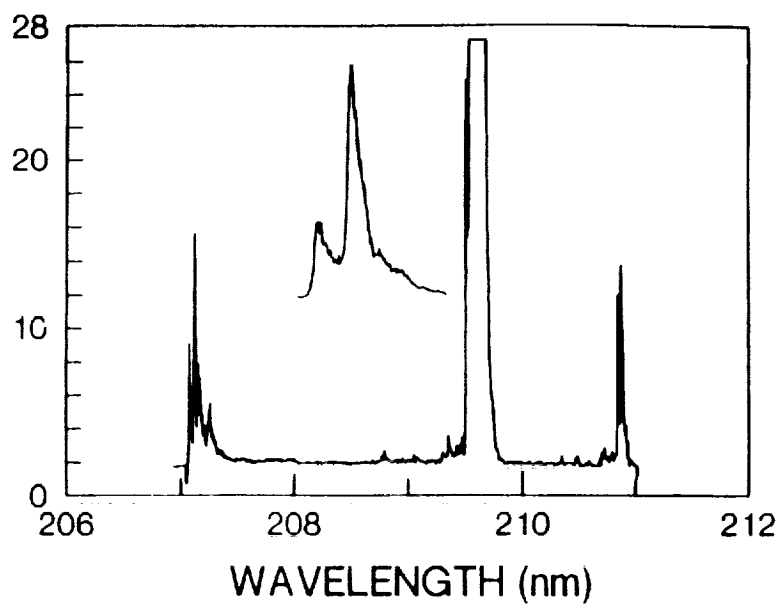


Figure 7

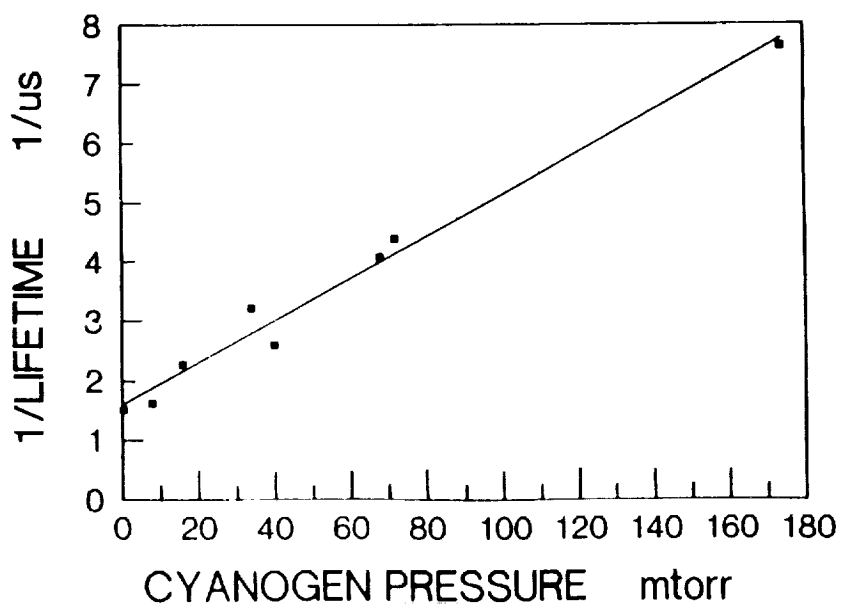


Figure 8

Figure 9 shows the fragment yield spectrum between 200 and 202 nm corresponding to excitation of the $1_0^2 4_0^1$ transition. The right hand half of Figure 10 shows the emission spectrum in the $1_0^2 4_0^1$ region as compared to that from the 4_0^1 region. There is a factor of several thousand difference in the intensities of the emissions.

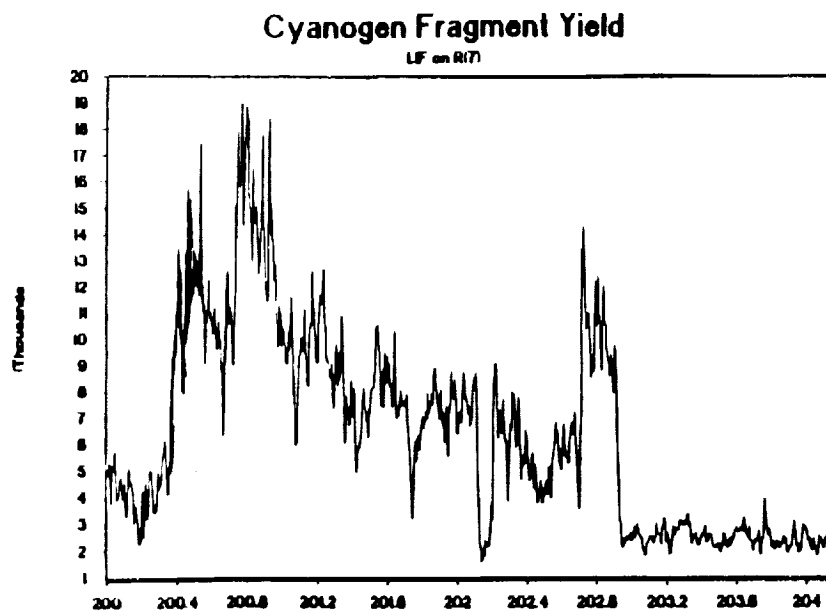


Figure 9

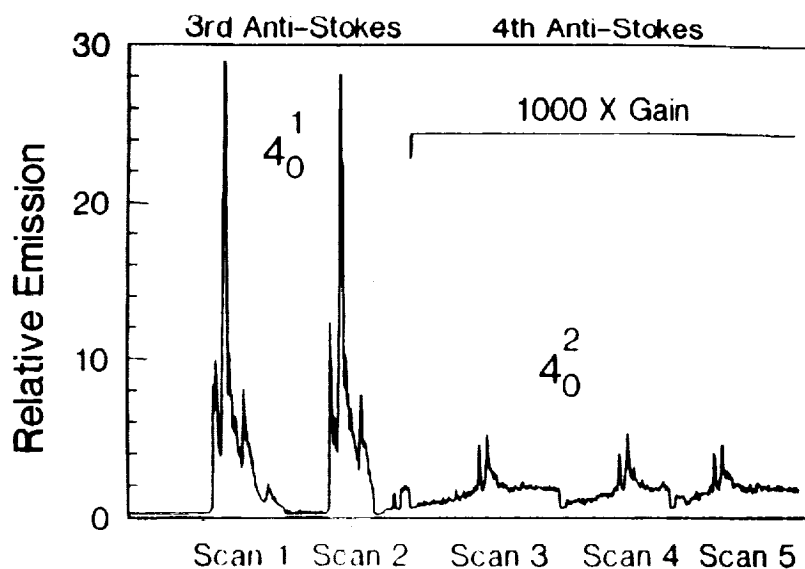


Figure 10

Discussion

Figure 11 is a linear correlation diagram from Reference 4. These observations can be qualitatively explained with the following model: $C_2 N_2$ is excited from the ground $X^1\Sigma^+$ state into the $A^1\Sigma^-$ state. At excitation energies below the dissociation limit the molecule simply fluoresces and returns to the ground state. This is shown conclusively by the fluorescence spectrum as explained in Reference 1. After excitation above the dissociation limit there is a competition between fluorescence, dissociation (where energetically possible) and crossing over to a lower triplet system. Emission can also occur from this triplet system back down to the ground state. The correlation diagram indicates that the $A^1\Sigma^-$ state cannot directly dissociate to ground state CN fragments in the linear configuration. While this restriction would be relaxed in a bent configuration it is also possible that dissociation occurs through a crossing to the $a^3\Sigma_u^+$ system which correlates with ground state fragments. The barrier in the linear configuration can be avoided if the molecule bends.

Future experiments will attempt to elucidate this mechanism and add quantitative detail to this qualitative model. Experiments to be done include measurement of the fluorescence spectra below the dissociation limit. This will allow us to elucidate the mechanism of dissociation. Second, we will compare the intensity of emission with that from known pressures of NO, allowing us to calculate quantum yields for all processes. This will allow us to map the state density of the emitting triplet state and provide a clock for measuring photodissociation rates.

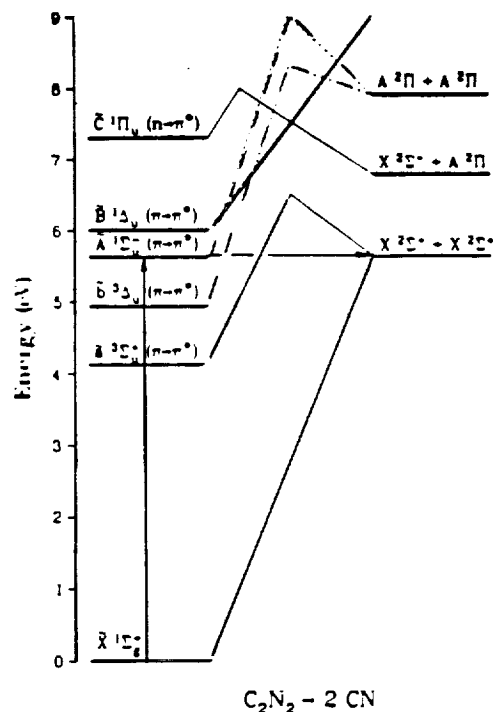


Figure 11

Conclusion

The study of cyanogen $C_2 N_2$ photolysis has produced several important results. First, significant emission was observed from $C_2 N_2$ following excitation to both bound and unbound states. This emission has not previously been reported. If, as has been suggested, cyanogen is a minor constituent of astronomical objects the intensity of this emission would be the measure of the cyanogen concentration. Second, we made initial measurements of the competition between emission and dissociation.

Acknowledgments

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